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POSSIBLE TRANSPORT OF VOLATILE TRACE ELEMENTS IN METEORITE PARENT BODIES

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Abstract: Transportation of volatile trace elements such as Bi, Tl and In in chondrite parent bodies was studied by computer simulation. Experimentally determined gas permeability of chondrites and a plausible thermal history of a parent body was used in the calculation. The effect of a carrier gas was found to be insignificant. Within the uncertainty of the thermodynamic data, fractionation of these volatile trace elements during thermal metamorphism is possible. More accurate thermodynamic data are required to settle the issue whether the fractionation of volatile trace elements was due to a nebula condensation process or due to thermal metamorphism in a parent body.

1. Introduction

Concentrations of volatile trace elements such as Bi, Tl and In in chondrites decrease with increasing metamorphic grade (type 3 to type 6). It has been debated whether this fractionation was due to a nebula condensation process (LARIMER and ANDERS, 1967; TAKAHASHI *et al.*, 1978) or due to the metamorphism in parent bodies (DODD, 1969). We examined the latter possibility in this study, by simulating the transport of volatile trace elements.

In earlier papers (SUGIURA *et al.*, 1984, 1986b) we studied possible transport of carbon in meteorite parent bodies. Our latest model (SUGIURA *et al.*, 1986b) takes into account a realistic thermal history and a gas permeability profile of the parent body. The following are the main features of the model. 1) A parent body was modelled by a layered sphere with a relatively low thermal conductivity ($K=3200(880+0.15T-1.5E7/T^2)\times(9.5E-8+3.15E-5/T+2.0E-17T^3)$, where T is temperature) in the solid interior, and a particulate insulating layer ($K=3.5E-3+7.3E-11T^3$) near the surface. 2) Radiogenic heat sources including ^{26}Al were assumed. The amount of ^{26}Al was adjusted to produce the maximum temperature 1200 K at the center. 3) Isotope systems of Ar and Sr were assumed to close in 100 Ma. 4) The proportion of type 3–6 materials, assigned by the maximum temperature reached during metamorphism, was

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similar to that observed in ordinary chondrites. From these conditions, the radius of the parent body was restricted to 30–50 km. 5) The gas permeability of a parent body was estimated from the gas permeability of chondrites (SUGIURA *et al.*, 1986a; MATSUI *et al.*, 1986). Two models of gas permeability were examined. In model A, the gas permeability of a chondrite with almost no cracks ($K_p=(1-0.0014P_c)\times(0.55+0.405T/298P)$, where P_c is a confining pressure, P is a gas pressure and K_p is in millidarcy) was used throughout the parent body. In model B, the permeability was increased (up to 10 times) near the surface in order to account for the formation of cracks due to impacts, and 6) Carbon was transported as carbon monoxide produced by the reaction of carbon with olivine.

In this paper we adopt a similar model and study the transportation of volatile trace elements Bi, Tl, In, Cd and Pb.

2. Vapour Pressures of the Volatile Trace Elements

In this paper, vapourization process is assumed to be the reverse of the condensation process studied by LARIMER (1973). The elements vapourized from interior were allowed to condense near the surface as their partial pressures exceeded their vapour pressures. The trace elements exist either as pure phases (metal or sulfide) or as solid solutions (in metallic iron or troilite). Their vapour pressures depend strongly on the presence of their pure phases. This, in turn, depends on the solubility of the elements in solid solution (LARIMER, 1973). Table 1 shows the relative volatility of the trace elements, defined by the ratio of the amount of an element in the vapour phase to that in the starting solid material. The heat of solution from LARIMER (1973) was used to calculate the relative volatility in the case when an element is in solid solution. The type I carbonaceous chondrite (CI) abundance of WASSON (1985) was used for the concentration in the starting material to calculate the relative volatility. Pure phases of Tl, Bi, In, and Cd are more volatile than carbon, but in solid solution they are less volatile (In is more volatile at 1000 K but becomes less volatile at higher temperatures). In our previous calculation on carbon transport (SUGIURA *et al.*, 1986b), it was shown that carbon can be transported during metamorphism if rather stringent conditions

Table 1. Relative volatility of some trace elements.

	Reaction	H_s (KJ/mol)	M_v/M_s at 1000 K	
			Solid solution	Pure phase
Tl	Tl(s)=Tl(g)	58.8	1.1×10^{-4}	1.9×10^{-1}
Bi	Bi(s)=Bi(g)	63.0	2.0×10^{-5}	2.9×10^{-2}
Pb	Pb(s)=Pb(g)	63.0	1.6×10^{-5}	1.0×10^{-3}
In	Fe+2InS=FeS+In_2S(g)	79.8	1.1×10^{-2}	8.7×10^{-1}
Cd	Fe+CdS=FeS+Cd(g)	37.8	6.5×10^{-4}	1.1
Zn	Fe+ZnS=FeS+Zn(g)	—	—	2.1×10^{-6}
C	C+Olivine=Fe+SiO_2+CO	—	—	2.3×10^{-3}

H_s is the heat of solution from LARIMER (1973). M_v is the amount of the element in the vapour phase and M_s is that in the starting solid material. (s) and (g) denote solid and gas phases, respectively. Vapor pressures of pure phases are calculated using the data in KUBASCHEWSKI and ALCOCK (1979) and LARIMER (1973).

were met. We expect that transport of these elements (In, Bi etc.) would be even more difficult if the heat of solution data are correct. (It seems impossible to transport Zn, because even the pure phase has a much smaller vapour pressure than carbon). The heat of solution of these volatile elements are, however, very poorly determined (WOOLUM and BURNETT, 1981). For instance, the heat of solution of Pb in Fe was referred to as 96.6 KJ/mol (LARIMER, 1973), but more recent data (JONES and HART, 1984) suggests a value of about 134.4 KJ/mol. In the present study the heat of solution was adjusted to the value required for the transport of volatile elements.

3. Carrier Gas

The trace elements could be transported by a carrier gas if there were a major gas phase. The effect of such a carrier gas (carbon monoxide) was examined. The role of a carrier gas is appreciable if the flow is viscous, *i.e.* at high pressures and/or in large cracks. In the case of a two component flow consisting of a major gas phase and a trace element, the Darcy's law for the trace element may be approximated by:

$$V=(K_1/\eta)\,\mathrm{d}p_1/\mathrm{d}r+(K_2/\eta)\,\mathrm{d}p_2/\mathrm{d}r\,, \tag{1}$$

where η is viscosity which is assumed to be the same for both gases. Subscripts 1 and 2 denote the carrier gas and the trace element gas, respectively. The first term denotes the flow of the trace element gas due to the carrier gas. The second term is the flow of the trace element gas due to its pressure gradient. The permeability can be written as

$$K=A+BT/p\,, \tag{2}$$

where A and B are constants determined by laboratory experiments (SUGIURA *et al.*, 1986a), T is temperature and p is the gas pressure. The first term in eq. (2) represents viscous flow and the second term denotes molecular flow. Since trace elements are carried only by viscous flow K_1 equals to A, but K_2 equals to $A+BT/p$. The carrier gas effect becomes important when the first term in eq. (1) is larger than the second.

4. Results

The thermal history of a parent body was determined by a numerical solution of the thermal conduction equation. Then, the Darcy's law, the continuity equation and the equation of state for an ideal gas were solved simultaneously (see SUGIURA *et al.*, 1986b). The variables used in the calculation are summarized in Table 2 and the resulting concentration profiles of the trace elements are shown in Figs. 1–5. In most cases, the carrier gas was not considered and model B was used. In all calculations, the initial concentration is 10% of CI abundance, and the radius of the parent body is 40 km. As the trace elements recondense near the surface (it was assumed that they did not escape from the surface), their concentrations approach to that observed in type 3 chondrites. The relative abundance as a function of radial distance shown in the figures are not sensitive to the initial concentration.

The effect of the gas permeability can be seen in Figs. 1a and 1b, where Tl concentrations are shown for model A and model B. The heat of solution (H_s) is 100.8 KJ/mol. In model A the fractionation among type 3–6 materials is about one order of

Table 2. Variable parameters used in the calculation.

Element	H_s*	Carrier gas	Gas permeable	Result
Tl	100.8*2	no	model A	Fig. 1a
Tl	100.8*2	no	model B	Fig. 1b
Tl	96.6*2	yes	model B	Fig. 1c
Tl	96.6*2	no	model B	Figs. 1d & 6
Bi	113.4*2	no	model B	Figs. 2a & 6
Bi	98.7*1	no	model B	Fig. 2b
Pb	126.0*2	no	model B	Fig. 3a
Pb	96.6*1	no	model B	Fig. 3b
In	96.6*2	no	model B	Figs. 4a & 6
In	79.8*1	no	model B	Fig. 4b
Cd	63.0*2	no	model B	Figs. 5a & 6
Cd	37.8*1	no	model B	Fig. 5b

* Heat of solution in KJ/mol.
*1 Heat of solution referred in LARIMER (1973).
*2 Heat of solution, rather arbitrarily chosen to produce substantial fractionation.

magnitude, whereas in model B a fractionation of more than three orders of magnitude is produced. In model B type 4 and 5 materials have smaller amount of volatiles than type 6 materials.

Figures 1c and 1d show the Tl concentration (for H_s=96.6 KJ/mol) with and without the carrier gas (CO), respectively. The effect of the carrier gas can be seen by comparing the corresponding profiles of the figures at 4 and 8 Ma. The broad minima in Fig. 1c are the result of rapid transportation of the trace element carried out by CO. The trace element recondenses near the surface, creating maxima. The profiles after about 16 Ma are not affected significantly by the carrier gas, since CO is exhausted by that time (SUGIURA *et al.*, 1986b). The net effect of the carrier gas is to reduce the concentration in the deep interior by about 50%. The effect of the carrier gas depends on the choice of the gas permeability. In our models, the permeability due to cracks are assumed to be small. However, if large scale cracks were dominant, the carrier gas could have an appreciable effect.

As shown in Figs. 1–5, the heat of solution for Tl, Bi, Pb, In and Cd required to produce adequate fractionation among type 3–6 materials are (without a carrier gas and for model B) about 100, 110, 120, 100 and 60 KJ/mol, respectively. These values are higher than those suggested by LARIMER (1973). If his values (Figs. 4b, 5b) or values estimated for metallic iron (Figs. 2b, 3b) are used, only type 4 and type 5 materials would be partially depleted in trace elements. As already mentioned, the heat of solution of the trace elements is poorly known. The heat of solution of Pb in Fe could be as high as 134.4 KJ/mol according to the new data by JONES and HART (1984). The heat of solution of Bi is not well determined (WOOLUM and BURNETT, 1981). There are no available data on Tl, In and Cd solid-solutions in Fe or FeS, although LARIMER (1973) suggested that a value as high as 126 KJ/mol would not be surprising for In. If such a rather high value of H_s is correct, transportation of volatile trace elements in parent bodies could have caused substantial fractionation of these elements among type 3–6 chondrites.

Figure 6 shows concentration profiles at 100 Ma of Tl (H_s=96.6 KJ), Bi (H_s=

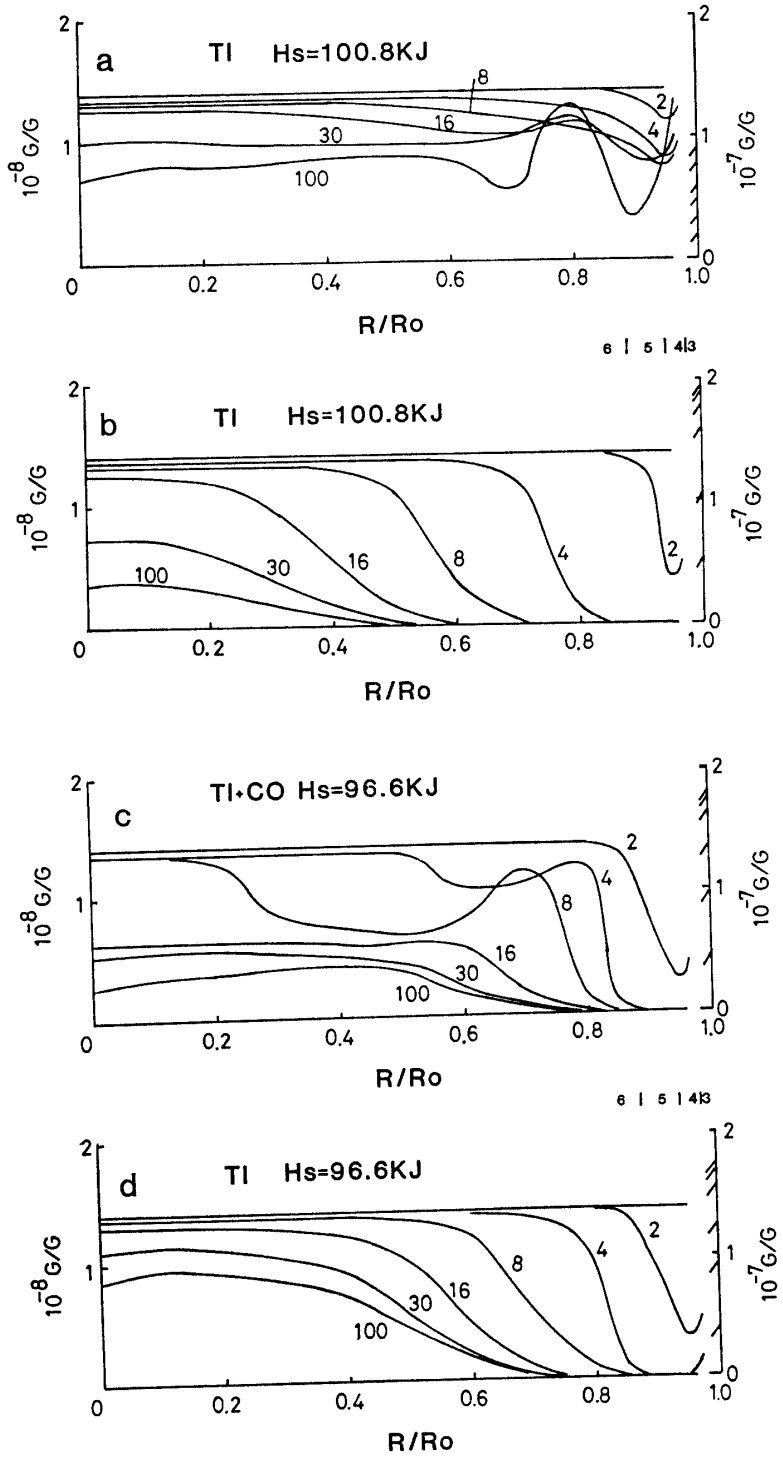

Fig. 1. Concentration of Tl as a function of normalized radial distance (R/R_0). R_0=radius of the parent body and R=distance from the center. Boundaries between type 3, 4, 5 and 6 materials are indicated at the top of bottom figures. Numbers on the curves are time in million years since the formation of parent body. Note the different scale at the surface, where concentrations increase with time monotonically. a) Heat of solution=100.8 KJ/mol and model A gas permeability was used. b) The same condition as (a) but for model B gas permeability. c) Concentration of Tl for heat of solution=96.6 KJ/mol and model B. The presence of the carrier gas (CO) is assumed. d) The same condition as (c) but the carrier gas is not present.

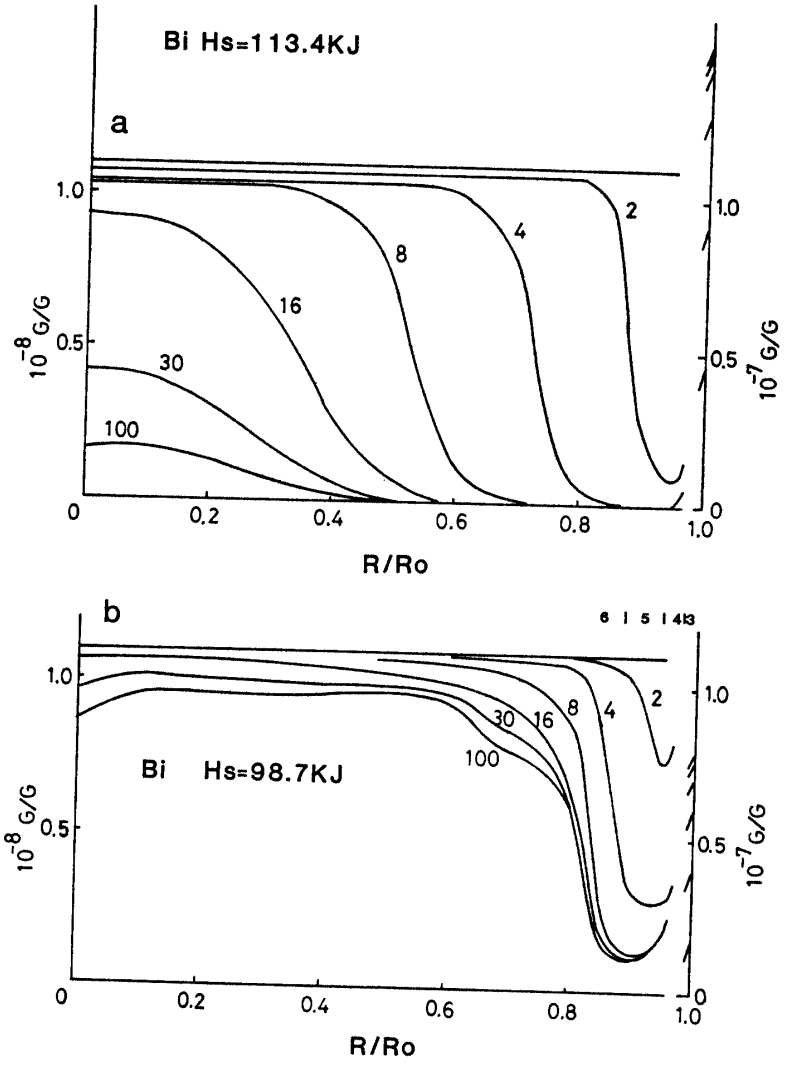

Fig. 2. Concentration of Bi for a) heat of solution=113.4 KJ/mol and b) heat of solution= 98.7 KJ/mol.

113.4 KJ), In (H_s=96.6 KJ) and Cd (H_s=63 KJ) on logarithmic scale. (The profile for Pb (H_s=126 KJ) is not shown because its fractionation is too large (log (C/Co)< −7) to be incorporated on the diagram.) The profiles for Tl, Bi and Cd are similar. Detailed comparison of the fractionation between elements is rather meaningless because it strongly depends on the choice of H_s. In shows a different profile because its vapour pressure has a different temperature dependence. Contrary to the observations on type 4–6 chondrites, the calculated volatile element concentrations decrease from type 6 to type 4 materials. This is partly due to the choice of the large gas permeability near the surface, which removes trace elements form type 4 and 5 materials efficiently. The high concentrations of these elements near the center indicate that the central part of a 40 km parent body is nearly a closed system for these elements with the assumed heat of solution. It seems that, to produce a concentration profile conformable with the observed trace element concentration in ordinary chondrites, we need (1) a slightly smaller parent body, (2) a smaller gas permeability near the surface than the one assumed in the model B, and (3) a high value of H_s.

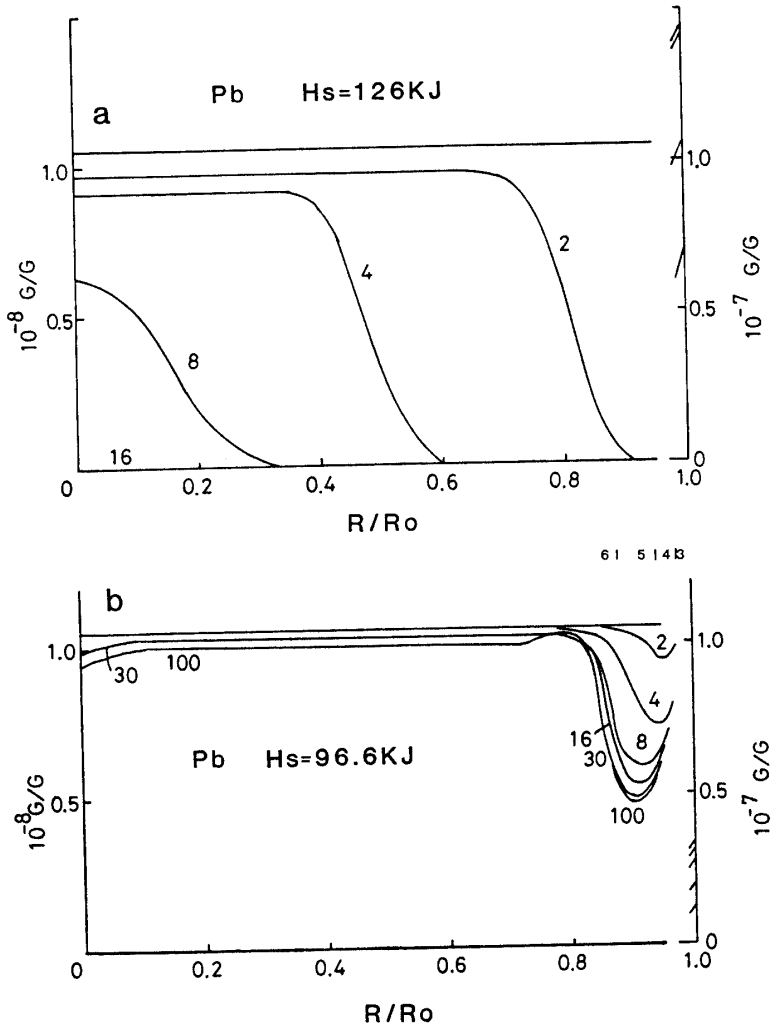

Fig. 3. Concentration of Pb for a) heat of solution=126 KJ/mol and b) heat of solution=96.6 KJ/mol.

5. Discussion and Conclusions

In laboratory heating experiments (IKRAMUDDIN *et al.*, 1977), trace elements such as In, Bi and Tl are very volatile. A substantial fraction of these elements is lost from a sample by heating to 1000°C for one week. Our simulation of transportation of these elements showed that the transportation inside a parent body is not as easily accomplished as the laboratory experiments suggest. This is partly because of the small permeability of the parent body and partly because the trace elements exists as solid-solutions which have lower vapor pressures. The effect of permeability is apparent even in laboratory experiments. Powder samples lose volatile elements more easily than small chip samples (IKRAMUDDIN and LIPSCHUTZ, 1975). At the scale of meteorite parent bodies, the rate of volatile loss, which is controlled by the gas permeability of the parent body, is very slow. Nevertheless, parent bodies can be considered as open systems (within a time scale of 100 Ma) for carbon (SUGIURA *et al.*, 1986b), because the vapour pressure of CO is high. Trace elements such as In are more volatile

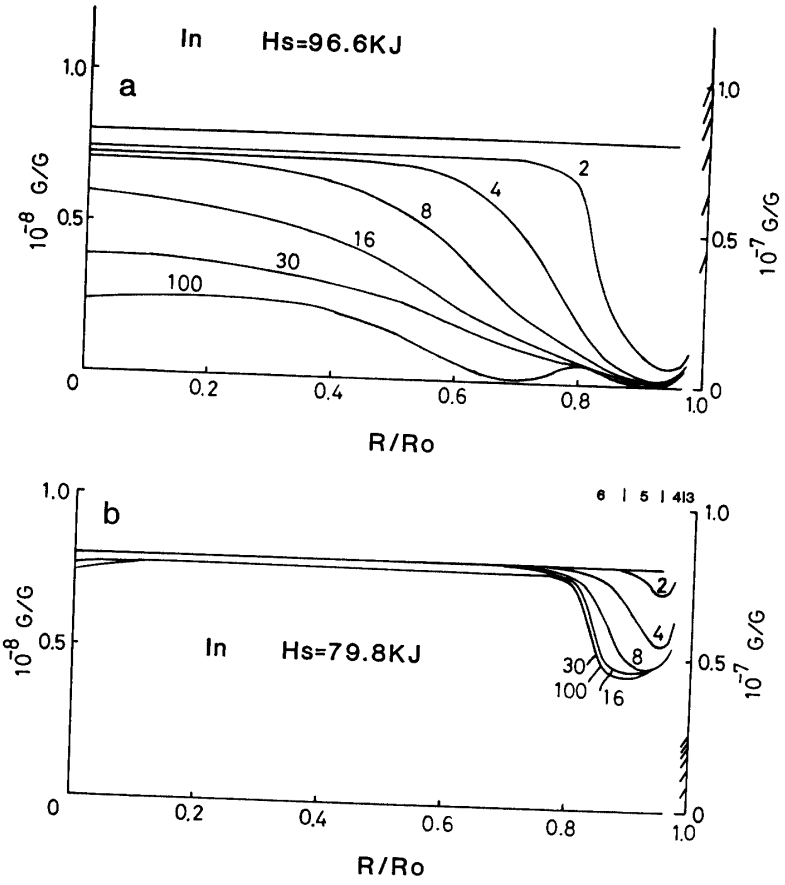

Fig. 4. Concentration of In for a) heat of solution=96.6 KJ/mol and b) heat of solution=79.8 KJ/mol.

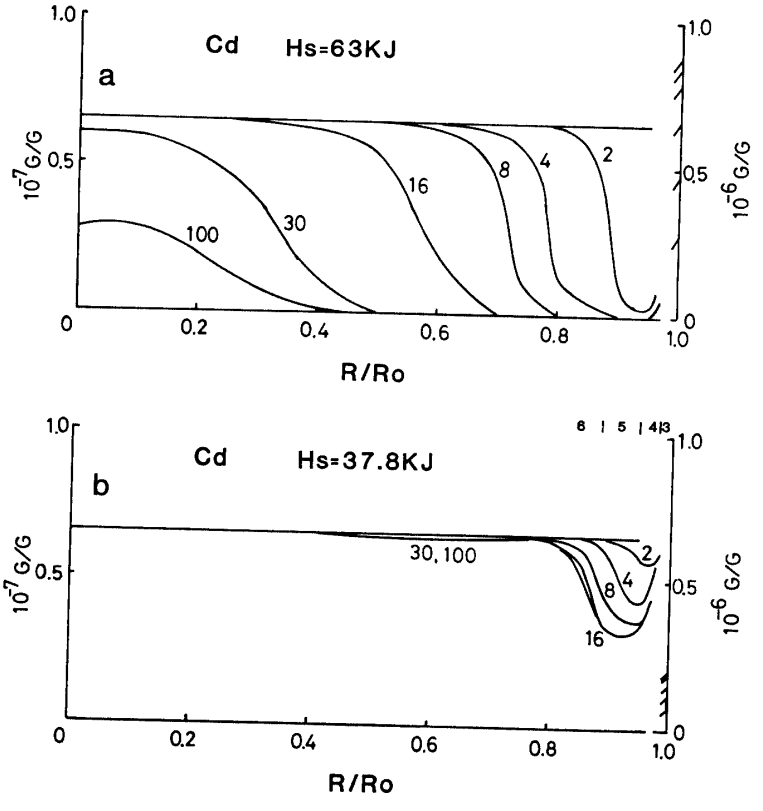

Fig. 5. Concentration of Cd for a) heat of solution=63.0 KJ/mol and b) heat of solution=37.8 KJ/mol.

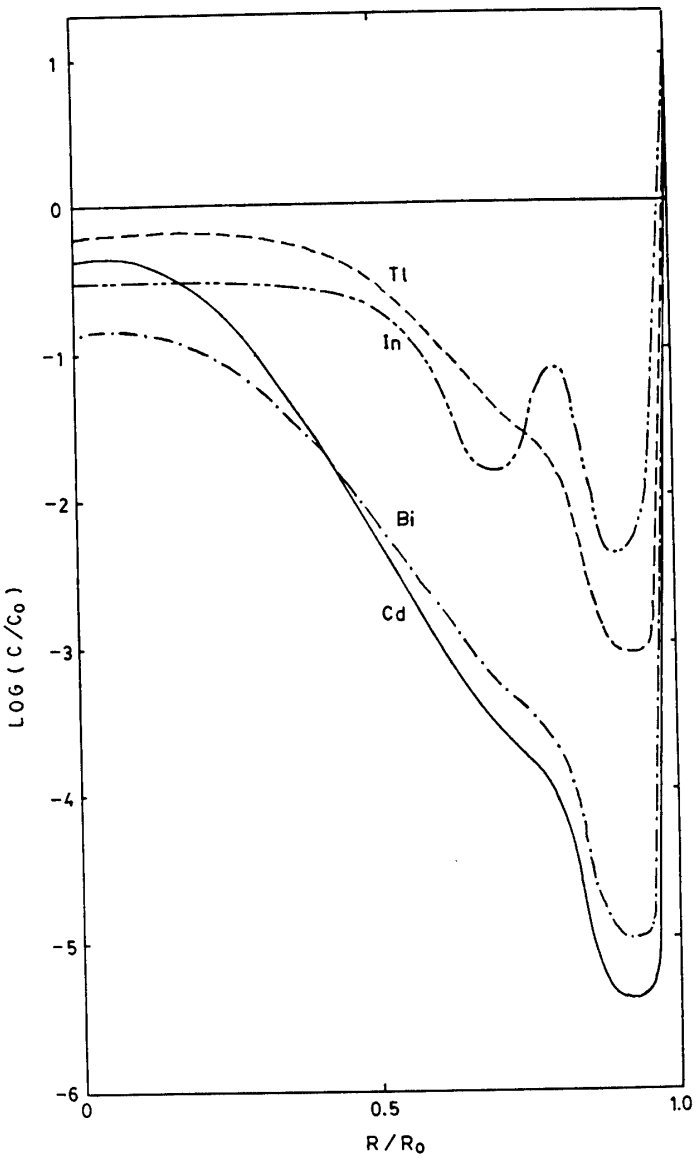

Fig. 6. Concentration of Tl, In, Bi and Cd at 100 Ma. Concentrations are normalized to the initial concentrations.

than carbon at low temperatures, where solubility in host phases is small and the elements exist as pure phases. As temperature increases, however, solubilities increase and all the elements enter solid-solutions and pure phases disappear. The solid-solutions have much lower vapour pressures than the pure phases. The presence of a carrier gas is not very effective in transporting trace elements. Available data for heat of solution are very poor in quality. Until more accurate thermodynamic data become available, the cause of fractionation of volatile trace elements cannot be understood properly.

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